Solutions Problem Set 1 Physical Chemistry II

Dr. Chatfield, Spring 2009

1 a) $\frac{dV}{dx} = \frac{d}{dx}\left[k\frac{x^2}{2}\right] = kx$

$$\frac{dx^2}{dt^2} = -\frac{1}{m}\frac{dV}{dx} \Rightarrow \boxed{\frac{dx^2}{dt^2} = -\frac{k}{m}x}$$

b) $\frac{d^2x}{dt^2} = \frac{d^2}{dt^2}\left[A\cos Bt\right] = -AB^2\cos Bt = -\frac{k}{m}x = -\frac{k}{m}A\cos BT$

$$\Rightarrow B^2 = \frac{k}{m} \quad \boxed{B = \sqrt{\frac{k}{m}}}$$

c) $T = \frac{m}{2}\left(\frac{dx}{dt}\right)^2 = \frac{m}{2}\left(\frac{d(A\cos Bt)}{dt}\right)^2 = \frac{m}{2}A^2\overset{B^2=\frac{k}{m}}{B^2}\sin^2 Bt$

$$V = \frac{k}{2}x^2 = \frac{k}{2}A^2\cos^2 Bt$$

$$E = T + V = \frac{m}{2}A^2\frac{k}{m}\sin^2 Bt + \frac{k}{2}A^2\cos^2 Bt$$

$$= \frac{k}{2}A^2\left(\overbrace{\sin^2 Bt + \cos^2 Bt}^{1}\right) = \frac{k}{2}A^2$$

$$\boxed{E = \frac{1}{2}kA^2 \text{ independent of time}}$$

2 $\overset{0.42\,eV}{T_{max}} = h\overset{\nu = \frac{c}{\lambda}}{\nu} - \Phi_0 \qquad \Phi_0 = h\nu_0$

$$\Phi_0 = h\nu - T_{max} = \frac{hc}{\lambda} - T_{max} = \frac{(6.626\times10^{-34}\,Js)(2.99\times10^{8}\,ms^{-1})}{254\times10^{-9}\,m} - 0.42\,eV$$

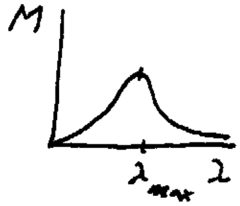
$$= 7.80\times10^{-19}\,J - 0.42\,eV\,(1.60218\times10^{-19}\,J/eV) = 7.13\times10^{-19}\,J = \boxed{\Phi_0 = 4.45\,eV}$$

$$\nu_0 = \frac{\Phi_0}{h} = \frac{7.13\times10^{-19}\,J}{6.626\times10^{-34}\,Js} = 1.07561\times10^{15}\,s^{-1} \quad \boxed{\lambda_0 = \frac{c}{\nu_0} = 278\,nm}$$

unimportant as $\lambda \to \infty$

3 a) $\lim_{\lambda\to\infty} M = \lim_{\lambda\to\infty} \frac{2\pi h c^2}{\lambda^5}\left(e^{hc/\lambda kT}-1\right)^{-1} = \lim_{\lambda\to\infty} \frac{2\pi h c^2}{\lambda^5}\left(1+\frac{hc}{\lambda kT}+\dots-1\right)^{-1}$

$$= \frac{2\pi k T c}{\lambda^4}$$

b) 

$\frac{dM}{d\lambda} = 0$ at $\lambda = \lambda_{max}$

$$0 = \frac{dM}{d\lambda} = \frac{d}{d\lambda}\left[\frac{2\pi h c^2}{\lambda^5}\left(e^{hc/\lambda kT}-1\right)^{-1}\right]$$

$$0 = -5\lambda^{-6}\left(e^{hc/\lambda kT}-1\right)^{-1} + \lambda^{-5}e^{hc/\lambda kT}\left(e^{hc/\lambda kT}-1\right)^{-2}$$

$\downarrow \times \lambda^7\left(e^{hc/\lambda kT}-1\right)^2$

$$0 = -5\lambda\left(e^{hc/\lambda kT}-1\right) + \frac{hc}{kT}e^{hc/\lambda kT}$$

$$\lambda = \frac{hc}{5kT}\,\frac{e^{hc/\lambda kT}}{e^{hc/\lambda kT}-1}$$

i) Approximate: $\frac{e^{hc/\lambda kT}}{e^{hc/\lambda kT}-1} \simeq 1$ (large λ) $\Rightarrow \lambda_{max} = \frac{hc}{5kT}$

ii) Better $\underbrace{\frac{\lambda kT}{hc}}_{\equiv x} = \frac{1}{5}\,\frac{e^{hc/\lambda kT}}{e^{hc/\lambda kT}-1} \Rightarrow \underbrace{x}_{LHS} = \underbrace{\frac{1}{5}\,\frac{e^{1/x}}{e^{1/x}-1}}_{RHS}$

initial guess: $x = \frac{1}{5} = 0.2 \Rightarrow$

LHS		RHS
0.2	$\rightarrow$	0.201357
0.201357	$\rightarrow$	0.201404
0.201404	$\rightarrow$	0.201405
0.201405	$\rightarrow$	0.201405 ✓

consistent

ITERATE UNTIL CONSISTENT

$x = 0.201405$

$\Rightarrow \lambda_{max} = \frac{hc}{kT}x$

$$\boxed{\begin{aligned} A_w = T\lambda_{max} &= 0.201405\,\frac{hc}{k} \\ &= 2.90\times10^{-3}\ mK \end{aligned}}$$

$r = \frac{d}{2} = \frac{1.391\times10^{6}\,\text{km}}{2}$

4 a) A = area of surface of sphere $= 4\pi r^2$

$\sigma = 5.67\times10^{-8}\,W\,m^{-2}K^{-4}$ $\quad T = 5800K$

$W = J s^{-1}$

M = intensity = energy per unit area per unit time

$$E/s = MA = \sigma T^4 A = 3.9\times10^{26}\,W$$

b) $E/s = mc^2/s \qquad m/s = \frac{E/s}{c^2} = 4.4\times10^{9}\,kg/s$

This is mass converted per second.

For the sun, $\Delta m = 4.00150 + 2(0.00055) - 4(1.00728)$
$= -0.02652$ amu for every
$4(1.00728) = 4.02912$ amu of ${}^1H^+$ consumed

Thus the total amount of hydrogen converted into Helium

$$m_{H^+} = 4.4\times10^{9}\,kg\,s^{-1}\left(\frac{4.02912}{0.02652}\right) = \boxed{6.6\times10^{11}\,kg\,s^{-1} = m_{{}^1H^+}}$$

c) $$\mathcal{E} = M(\lambda) = \int_0^\infty \frac{2\pi hc^2}{\lambda^5\left(e^{hc/\lambda kT}-1\right)}\,d\lambda$$

Define $x = \frac{hc}{\lambda kT} \Rightarrow \lambda = \frac{hc}{kT}x^{-1} \quad d\lambda = \frac{-hc}{kT}x^{-2}dx$

$$\mathcal{E} = 2\pi hc^2\left(\frac{kT}{hc}\right)^5\left(-\frac{hc}{kT}\right)\int_\infty^0 x^5\cdot x^{-2}(e^x-1)^{-1}dx$$

$$= +2\pi hc^2\left(\frac{kT}{hc}\right)^4 \underbrace{\int_0^\infty x^3(e^x-1)^{-1}dx}_{=\pi^4/15\ \text{(Table}} = 6.44\times10^{7}\,J\,m^{-2}s^{-1}$$

$$\mathcal{E} = \sigma T^4 \Rightarrow \boxed{\sigma = \frac{\mathcal{E}}{T^4} = 5.69\times10^{-8}\,J\,m^{-2}s^{-1}K^{-4}}$$

5 $\displaystyle\int_{300\,nm}^{400\,nm} M\,d\lambda \approx M_{\lambda}\,\Delta\lambda \qquad M_{\lambda} = 380\,nm$

$\Delta\lambda = 100\,nm$

$$M_{\lambda}\Delta\lambda = \frac{2\pi hc^2}{(350\,nm)^5}\left(e^{hc/kT(380\,nm)} - 1\right)^{-1} 100\,nm$$

$$= 7.62\times10^{6}\,W$$

$$f(300-400\,nm) = \frac{7.62\times10^{6}\,W}{\underset{5.67\times10^{-8}\,W\,m^{-2}K^{-4}}{\sigma}\,\underset{6000K}{T^4}} = \boxed{0.10 = f}$$